Electronic Supplementary Information (EIS)

Highly Stable Chiral Bimetallic Mesoporous Platinum-Ruthenium Electrodes for Enantioselective Recognition

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Experimental Procedures

Chemicals

R-mandelic acid ((R)-MA), S-mandelic acid ((S)-MA), hexachloroplatinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$), ruthenium(III) chloride hydrate ($RuCl_3 \cdot xH_2O$), and polyoxyethylene (20) cetyl ether ($HO(CH_2CH_2O)_{20}C_{16}H_{33}$, Brij® 58) were received from Sigma-Aldrich. Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were obtained from Alfa. MilliQ water (18.2 MΩ·cm at 25 °C) was employed for all experiments. All chemicals were used without further purification.

Synthesis of chiral-imprinted bimetallic mesoporous Pt-Ru electrodes

First, the electroplating mixture was prepared by mixing the metal salts (29 wt%), including 0.1656 g of $H_2PtCl_6 \cdot xH_2O$ and 0.0844 g of $RuCl_3 \cdot xH_2O$ (40 Pt: 60 Ru at%), and 0.3625 g of Brij® 58 (42 wt%). Then, the mixture was heated at 80 °C until the metal salts were homogeneously mixed with the non-ionic surfactant. At the same time, 0.0125 g of (S)-MA or (R)-MA (0.05 weight ratio of MA/metal salts), acting as a chiral template, was dissolved in 0.25 g of MilliQ water (29 wt%). Then, the MA solution was added to the electroplating gel. The gel was mixed vigorously, sealed in a vial, and subjected to three heating/cooling cycles between 40 °C for 45 min with constant heating and at 25 °C for 15 min. Finally, the electroplating gel was allowed to equilibrate at 40 °C before use. In the case of the non-imprinted mesoporous Pt-Ru electrodes, the preparation method was repeated as mentioned above, excluding the addition of MA template to the plating gel.

For electrodeposition, the plating gel was put on a gold-coated glass slide as a substrate. The electrochemical deposition was carried out with a three-electrode configuration using Ag/AgCl (sat. KCl), a Pt mesh (geometric area of 1 cm^2), and the gold-coated glass slide (geometric area of 0.25 cm^2) as a reference, counter and working electrodes, respectively, connected to a potentiostat (Metrohm μAutolab Type III). All recordings were analyzed using the Nova (version 2.0) software. Electrodeposition of the Pt-Ru electrodes was performed at 40 °C at -0.20, -0.15, and -0.10 V (Ag/AgCl) with injected deposition charge densities of 1, 2, 4, 6, and 8 C cm^{-2}.

Characterization of chiral-imprinted bimetallic mesoporous Pt-Ru electrodes

The Pt-Ru electrodes were physically and electrochemically characterized by several techniques. To determine the electrochemically active area, cyclic voltammetry (CV) was performed in 0.5 M H_2SO_4 at a scan rate of 100 mV s^{-1} until identical voltammograms were obtained. The surface morphology (both top-view and cross-sectional imaging) and the composition and dispersion of the elements of the Pt-Ru electrodes were monitored by Field Emission Scanning Electron Microscopy (FE-SEM) equipped with an Energy Dispersive X-ray spectrometry (FE-SEM/EDS) on a JEOL, JSM-7610F. Porosity of the ultra-thin Pt-Ru layers was examined by Transmission Electron Microscopy (TEM) with a JEOL JEM-ARM200F microscope at 200 kV. The alloy structure of Pt-Ru was determined by X-ray diffraction (XRD) on a Bruker D8 ADVANCE instrument with Cu Kα radiation at 40 kV and 40 mA using a thin-film analysis mode. The metallic state of the Pt-Ru was determined by X-ray Photoelectron Spectroscopy (XPS) performed on a JEOL JPS-9010 equipped with a monochromatic Al Kα source. Prior to analysis, Pt-Ru samples were pretreated with a low-energy electron flood gun. The C 1*s* peak at 284.7 eV was used as a reference to correct the positions of the other spectra. The depth profile analysis of XPS was carried out by etching the Pt-Ru films with an argon ion gun for 5 s at an etching rate of approximately 2.50 nm s^{-1}, meaning that the total removed sample layer was around 14 nm. Furthermore, elemental analysis by XPS was calculated using the relative integrated peak areas of the Pt 4*f* and Ru 3*d* and reported in atomic percentages (at%) unit.

Stability testing of chiral-imprinted bimetallic mesoporous Pt-Ru electrodes via enantioselective recognition

Chiral recognition was examined using (S)-MA or (R)-MA imprinted mesoporous Pt-Ru electrodes, produced with a deposition charge density of 4 C cm^{-2}. The study was carried out by Differential Pulsed Voltammetry (DPV) with the following parameters: step potential of 0.1 V, modulation amplitude of 0.05 V, modulation time of 0.5 s, interval time of 0.5 s, and a solution of 10 mM mandelic acid in 10 mM HCl as supporting electrolyte (pH 1.4). Before analysis, the solution was degassed by nitrogen bubbling for 30 min. The electrode potential was scanned from 0.2 to 0.8 V. CV scans in a 0.5 M H_2SO_4 solution with a scan rate of 100 mV s^{-1} were performed after the analysis to eliminate chiral information.

Enantioselectivity between (R)-MA and (S)-MA was calculated with the following the relationship

$$Enantioselectivity = \frac{A_S}{A_R} \quad \text{or} \quad \frac{A_R}{A_S} \tag{1}$$

with A_S and A_R being peak areas of either (R)-MA or (S)-MA DPVs integrated by OriginPro version 8.5.

Results and Discussion

Effect of deposition potentials

During the co-electrodeposition, the applied reduction potentials were varied from -0.20 to -0.15 and -0.10 V (vs. Ag/AgCl). FE-SEM images as shown in **Fig. S1** illustrate rough external surfaces with attached nanoparticles in the cases of highly negative potentials (-0.20 and -0.15 V), while applying -0.1 V leads to a smooth external surface. The distribution of Pt and Ru elements in the Pt-Ru films was analyzed by the FE-SEM/EDS (**Fig. S2**) and summarized in **Table. S1**. Applying different potentials results in a non-significant distribution of Pt and Ru elements of about 50 Pt:50 Ru at% in the deposited films. The elemental ratio of approximately 50 Pt:50 Ru at% improves the electrooxidation of alcohol compounds since Ru can supply oxygen atoms to the active Pt and the Ru itself has a carbon monoxide tolerance that can improve the electrochemical catalyst stability. [1]

The Pt-Ru layers were electrochemically characterized by cyclic voltammetry (CV) in a 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1}. Rough external surfaces of Pt-Ru can also be confirmed by cyclic voltammograms shown in **Fig. S3**. The CV curves reveal larger signals for more negative deposition potentials, implying a higher active surface area due to the rough outermost surface. The rough external surface of mesoporous metal films can introduce non-selective sites for electrochemical reactions, because the selective sites are located in the cavities of the mesopores. [19, 20] In order to decrease the influence of these unfavourable reaction sites, mesoporous Pt-Ru electrodes were generated at -0.10 V for further studies.

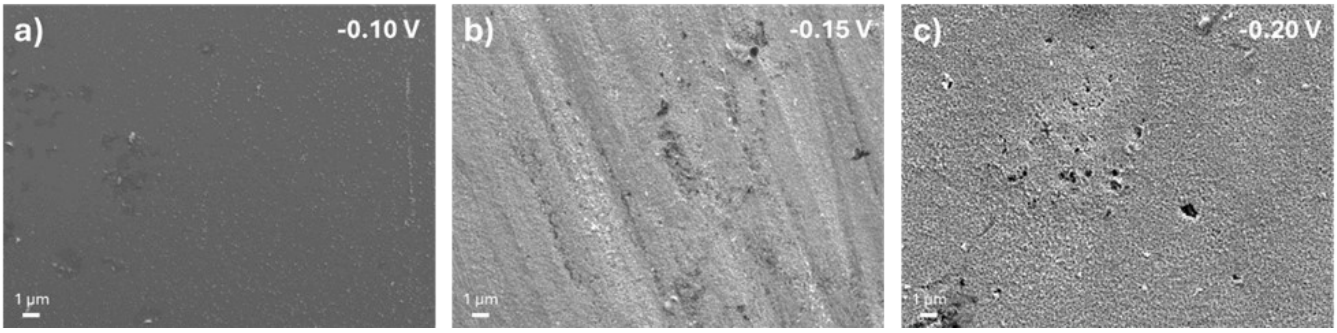


Fig. S1 Top-view FE-SEM images of mesoporous Pt-Ru electrodes obtained for different deposition potentials: a) -0.10 V, b) -0.15 V, and c) -0.20 V (vs. Ag/AgCl) with a controlled injected charge density of 4 C cm^{-2} (scale bar 1 µm).

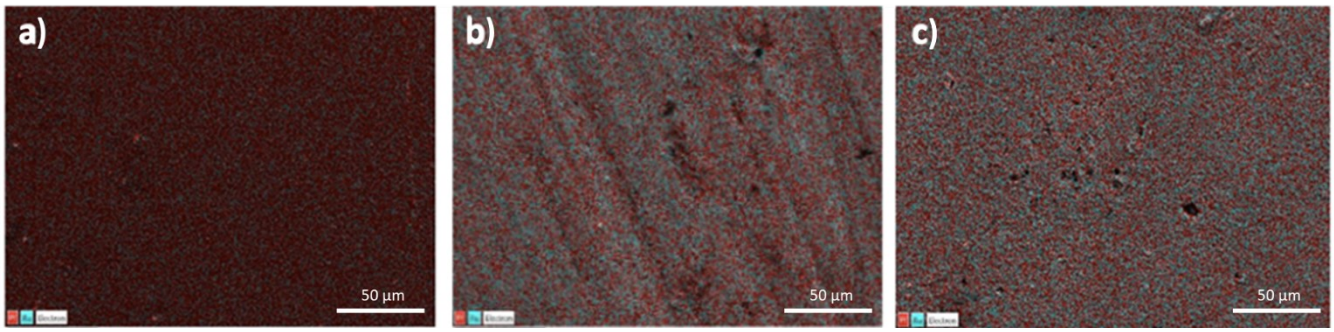


Fig. S2 FE-SEM/EDS analysis of the bimetallic Pt-Ru electrode prepared with different deposition potentials: a) -0.10 V, b) -0.15 V, and c) -0.20 V (vs. Ag/AgCl) with a controlled injected charge density of 4 C cm^{-2} (scale bar 50 µm, red and light blue colors represent Pt and Ru respectively).

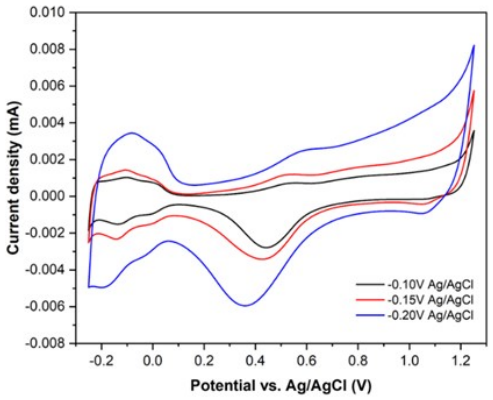


Fig. S3 Cyclic voltammograms of the bimetallic Pt-Ru electrodes prepared with different deposition potentials of -0.10 V (black), -0.15 V (blue), and -0.20 V (red) with an injected charge density of 4 C cm^{-2}. All data were obtained after 15 CV scans in 0.5 M H_2SO_4 at a scan rate of 100 mV s^{-1}.

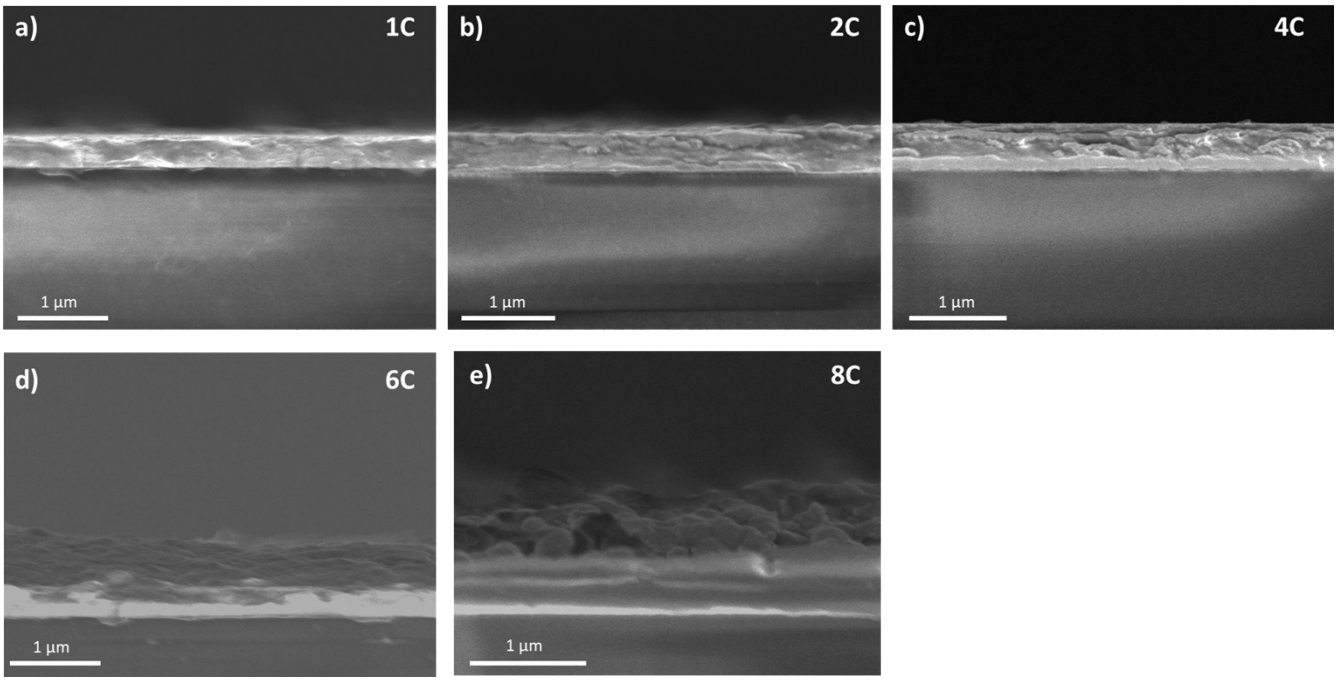


Fig. S4 Cross-sectional FE-SEM images of Pt-Ru films prepared with various injected charge densities: a) – e) Pt-Ru electrodes prepared with charge densities of 1, 2, 4, 6 and 8 C cm^{-2} at a deposition potential of -0.1 V.

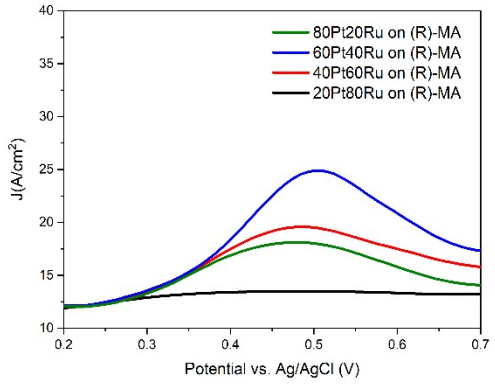


Fig. S5 Effect of Pt-Ru ratio in the plating mixture on the electrooxidation efficiency of R-MA.

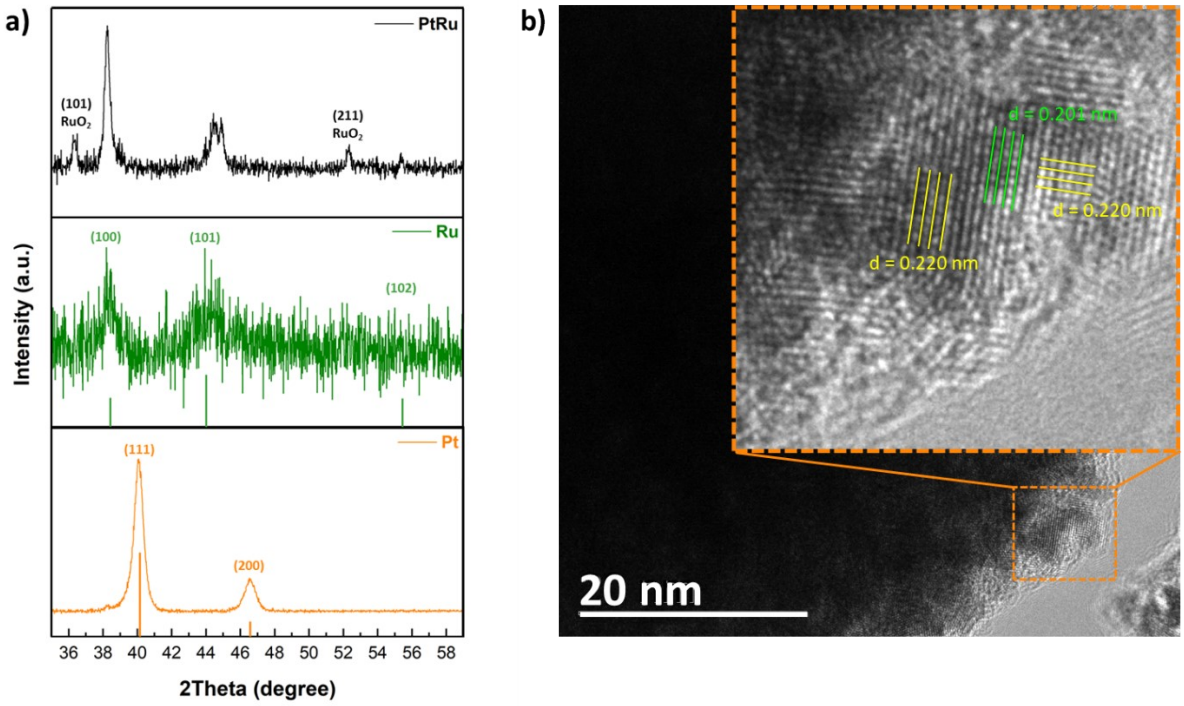


Fig. S6 Structural analysis of bimetallic Pt-Ru electrodes: a) XRD pattern of Pt, Ru and Pt-Ru films, and b) HR-TEM image of an ultra-thin Pt-Ru film.

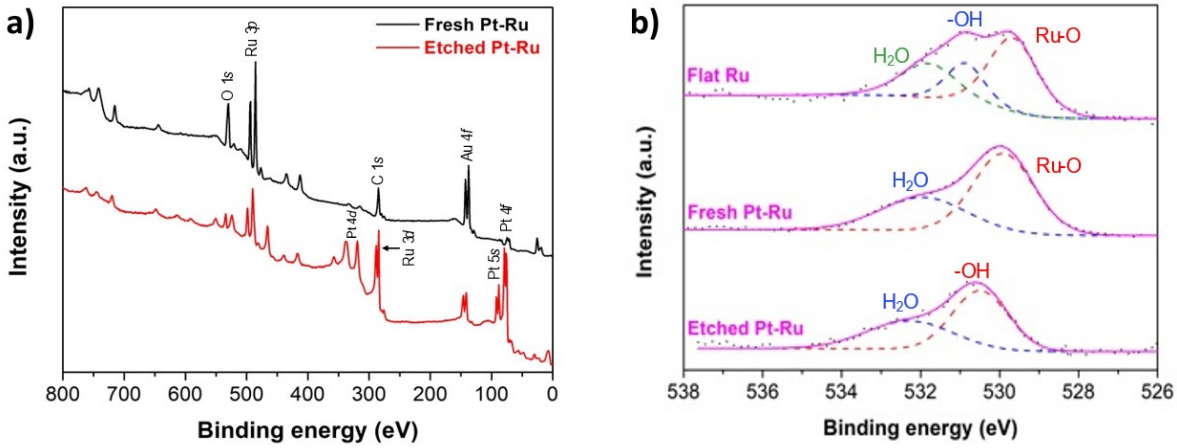


Fig. S7 Surface analysis of bimetallic Pt-Ru electrodes: a) Wide scan XPS spectra of fresh and etched Pt-Ru electrodes, and b) Narrow scan XPS spectra of flat Ru, as well as fresh and etched Pt-Ru electrodes in the region of O 1*s*.

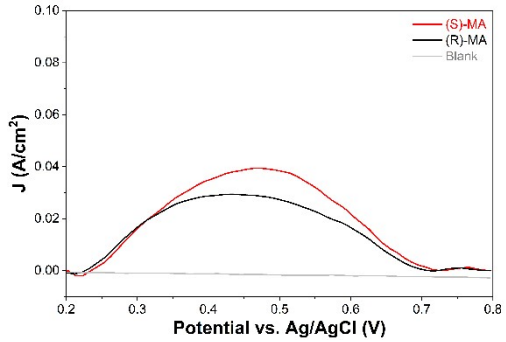


Fig. S8 Differential pulse voltammograms (DPVs) of the non-imprinted (N-imp) Pt-Ru electrodes. The experiments were conducted in 10 mM (R)-MA (black) and (S)-MA (red) dissolved in 10 mM HCl supporting (dash line, blank) electrolyte solution. All DPVs were plotted through the background correction. The enantioselectivity is approximately 0.9 ± 0.2.

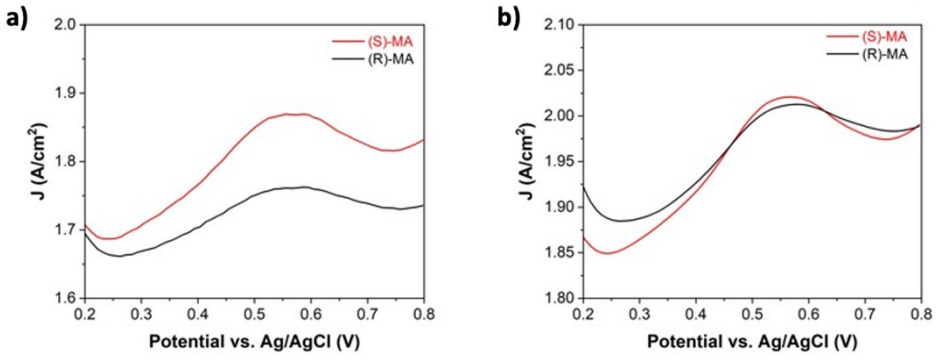


Fig. S9 Differential pulse voltammograms (DPVs) of the electrooxidation of MA with various (S)-MA imprinted (S-imp) Pt-Ru electrodes: a) and b) S-imp Pt-Ru electrodes after erasing chirality for 20 and 30 cycles, respectively. The experiments were performed in 10 mM (R)-MA (black) and (S)-MA (red) dissolved in 10 mM HCl supporting electrolyte solution. Erasing chiral information was achieved by CV scan from -0.25 to +1.40 V performed in 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1}.

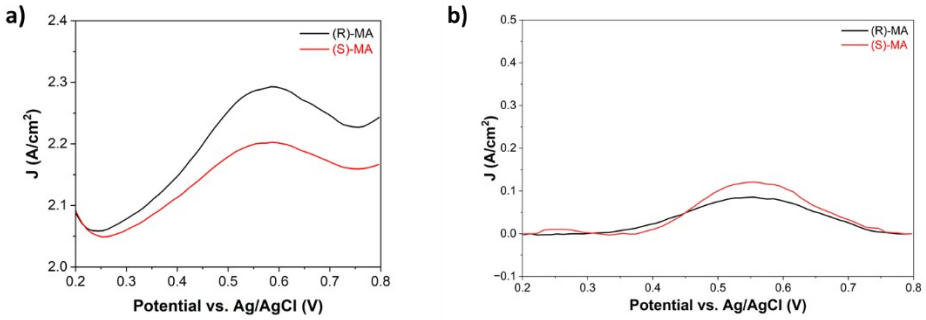
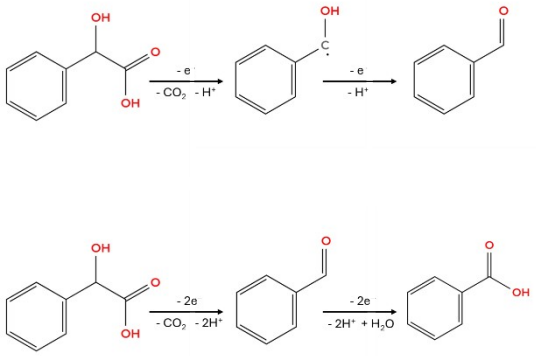


Fig. S10 Differential pulse voltammograms (DPVs) of the electrooxidation of MA with various (R)-MA imprinted (R-imp) Pt-Ru electrodes: a) and b) R-imp Pt-Ru electrodes after erasing chirality for 20 and 30 cycles, respectively. The experiments were conducted in 10 mM (R)-MA (black) and (S)-MA (red) dissolved in 10 mM HCl supporting electrolyte solution. Erasing the chiral information was achieved by CV scan from -0.25 to +1.40 V performed in 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1}.



Scheme. S1 Proposed mechanisms for the electrooxidation of mandelic acid via a two or four electron transfer. The figure was adapted from Ref. [2]

Table. S1 Elemental analysis on the surface of Pt-Ru electrodes obtained by EDS-SEM.

Applied Potentials (V vs. Ag/AgCl)	Pt (at %)	Ru (at %)
-0.20	45	55
-0.15	44	54
-0.10	50	50

Table. S2 The d-spacing information obtained by XRD.

2Theta (degree)	(hkl)	d-spacing (nm)
38.2	Ru (100)	0.235
44.0	Ru (101)	0.210
40.1	Pt (111)	0.225
46.5	Pt (200)	0.195
38.3	Pt-Ru	0.235
44.3	Pt-Ru	0.204

Table. S3 Relative peak areas of the different chiral recognition experiments with chiral imprinted electrodes extracted from DPVs. Peak areas of either (R)-MA or (S)-MA electrooxidation were integrated with OriginPro version 8.5.

Electrodes	Relative peak areas	
	(R)-MA/(S)-MA	(S)-MA/(R)-MA
(R)-MA Pt	2.5 ± 0.1	-
Erased (R)-MA Pt after 10 cycles	1.0 ± 0.1	-
(R)-MA Pt-Ru	7.1± 0.1	-
Erased (R)-MA Pt-Ru after 10 cycles	2.4 ± 0.7	-
Erased (R)-MA Pt-Ru after 20 cycles	1.2 ± 0.1	-
Erased (R)-MA Pt-Ru after 30 cycles	1.0 ± 0.2	-
(S)-MA Pt-Ru	-	6.0 ± 1.0
Erased (S)-MA Pt-Ru after 10 cycles	-	2.7 ± 0.2
Erased (S)-MA Pt-Ru after 20 cycles	--	1.7 ± 0.1
Erased (S)-MA Pt-Ru after 30 cycles		1.1 ± 0.1

References

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2 M. Borazjani, A. Mehdinia, A. Jabbari, *J. Electroanal. Chem.*, 2017, **805**, 83-90.